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(54) Keratotic plug remover

Entferner für keratöse Komedonen

Composition d'enlèvement de komedones kératiniques

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The file contains technical information submitted after the application was filed and not included in this specification

P92-183 EP

Prosecution History

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Description

BACKGROUND OF THE INVENTION

Field of the Invention:

The present invention relates to a keratotic plug remover which excellently removes keratotic plugs formed in the pores of the skin, and a method of removing keratotic plugs from the skin utilizing such a keratotic plug remover.

Discussion of the Background:

Having conspicuous pores in the skin is a serious skin problem, especially for women, and is mainly caused by keratotic plugs formed in the pores of the skin. Keratotic plugs are dead epidermal cells keratinized together with sebaceous matters and dirt which plug the pores of the skin. If proper treatment is not given, not only conspicuous pores but also various skin troubles result. Accordingly, removal of keratotic plugs is advisable in view of the health and beauty of the skin.

Ordinary face detergents, make-up removers, however, cannot sufficiently remove the keratotic plugs.

The use of various anionic or non-ionic polymers for skin treatment is known (EP-A-323 652; US-A-4,126,142; JP-A-55127312; JP-A-6335511; JP-A-6357508; GB-A-2 144 133).

Pack preparations, which are applied to the skin and peeled off after dried, and which generally contain an anionic or nonionic polymer such as polyvinyl alcohol and polyvinyl pyrrolidone as a major component of a film forming agent, are still not sufficiently effective for removing dirt from the skin pores and especially for removing keratotic plugs.

Thus, there remains a need for a keratotic plug remover which can effectively remove keratotic plugs formed in the pores of the skin and a method of removing keratotic plugs from the skin utilizing such plug removers.

SUMMARY OF THE INVENTION

Accordingly, it is one object of the present invention to provide novel keratotic plug removers which effectively remove keratotic plugs from the skin.

It is another object of the present invention to provide a method for removing keratotic plugs from the skin which utilized such keratotic plug removers.

These and other objects are achieved by the keratotic plug remover of claim 1.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The salt forming group of the polymer which is useful in the present invention is not particularly limited as long as it can form a salt in the presence of an acid or a base, and anionic, cationic and amphoteric groups are suitable. Examples of the salt forming group are carboxyl, sulfonic acid group, sulfuric acid residual group ($-OSO_3H$), phosphoric acid residual group ($-OPO_3H_2$), nitric acid residual group ($-NO_2$), amino group, ammonium group, and the like. Two or more of these groups may be present in one compound.

The polymer compound which is useful in the present invention is preferably water-soluble from the viewpoint of good appearance, but it is not necessarily water-soluble for the purpose of achieving the effects of this invention. The compounds which are not water-soluble may take the form of dispersion and/or emulsion.

Examples of the polymers useful in the present invention include: hyaluronic acid, sodium hyaluronate, sodium chondroitin sulfate which are mucopolysaccharides; alginic acid, sodium alginate, ammonium alginate, sodium carboxylmethylcellulose, and carboxymethyl amylose which are hemicelluloses. These are of natural origin or semi-synthesized polymers. In this invention, synthesized polymers are more preferable. Examples of the synthesized polymers include (A) polymers of one or more monomers listed in (1) to (3) below, (B) copolymers of the monomers as listed in (1) to (3) and another monomer which has no salt forming group, such as vinyl esters of aliphatic carboxylic acid such as vinyl acetate, (meth)acrylic esters such as methyl methacrylate, alkyl vinyl ethers such as methyl vinyl ether, N-vinyl cyclic amides such as N-vinylpyrrolidone, styrene and alkyl-substituted styrene, and (C) mixtures of the above-mentioned polymers.

(1) Anionic monomers:

Acrylic acid (AA), Methacrylic acid (MA), Maleic acid, itaconic acid and the like, which are unsaturated carboxylic acid monomers or their anhydrides or their salts;

Styrene sulfonic acid, 2-Acrylamide-2-methyl propane sulfonic acid (AMPS) and the like, which are unsaturated sulfonic acid monomers or their salts;

Vinyl phosphonic acid, Acid phosphoxyethyl (meth)acrylate and the like, which are unsaturated phosphoric mono-

mers.

(2) Caticnic monomers

Dimethylaminoethyl acrylate (DMAEA), Dimethylaminoethyl methacrylate (DMAEMA), Dimethylaminopropylacrylamide (DMAPAAm), Dimethylaminopropyl methacrylamide (DMAPMAAm), and the like, which are (meth)acrylamides or (meth)acrylic acid esters having a dialkylamino group;

Dimethylaminostyrene (DMASt), Dimethyaminomethylstyrene (DMAMSt) and the like, which are styrenes having a dialkylamino group;

4-Vinyl pyridine, 2-vinyl pyridine and the like, which are vinyl pyridines;

Quaternarized products of these with a known quatenarizing agent such as alkyl halide, benzyl halide, alkyl or aryl sulfonic acid, or dialkyl sulfate.

(3) Amphoteric monomers

N-(3-sulfopropyl)-N-acryloyloxyethyl-N,N-dimethylammonium betaine, N-(3-sulfopropyl)-N-methacroylamidepropyl-N,N-dimethylammonium betaine, N-(3-carboxymethyl)-N-methacroylamidepropyl-N,N-dimethylammonium betaine, N-carboxymethyl-N-methacroyloxyethyl-N,N-dimethylammonium betaine.

When the salt forming group of these polymers is not ionized, it is preferred to ionize it via neutralization with known acids such as hydrochloric acid and sulfuric acid which are inorganic acids; acetic acid, propionic acid, lactic acid, succinic acid, glycol acid which are organic acids, or with known bases such as triethylamine, trimethylamine which are tertiary amines; ammonia; or sodium hydroxide.

Among the mentioned polymer compounds, preferred ones in view of the mildness to the skin and high effectiveness for removing keratotic plugs are polymers of one or more cationic monomers, copolymers between one of these polymers and an amphoteric monomer or a monomer having no salt forming groups, and mixtures of these polymers.

Preferable examples of the cationic monomers include dimethylaminoethylacrylate (DMAEA), dimethylaminoethylmethacrylate (DMAEMA), dimethylaminopropylacrylamide (DMAPAAm), dimethylaminopropyl methacrylamide (DMAPMAAm) and the like, which are (meth)acrylic esters or (meth)acrylamides having a dialkylamino group; and quaternary compound of them which are quaternarized with a known quaternarizing agent such as alkyl halide, benzyl halide, alkyl or aryl sulfonic acid or dialkyl sulfate. Among them, especially preferred are dimethylaminoethylmethacrylate (DMAEMA) and its quaternarized products; quaternarized products of dimethylaminopropyl methacrylamide (DMAPMAAm); polymers of one or more of these monomers; copolymers between one or more of these monomers and the above-mentioned monomers; and mixtures thereof.

The molecular weight (weight average) of these polymers is preferably in the range of from 10,000 to 1,500,000, and especially from 100,000 to 1,000,000. Molecular weights less than 10,000 will result in insufficient film strength and easily breakable films upon peeling-off. Polymers having a molecular weight over 1,500,000 are difficult to manufacture.

The preferable amount of the polymer to be incorporated into the keratotic plug remover preparation according to the invention is from 0.01 to 70% by weight, preferably 5 to 40% by weight based on the total weight of the preparation.

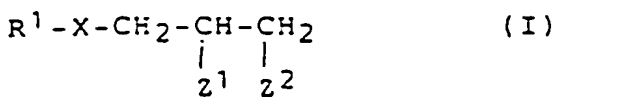
The above-mentioned synthesized polymers are used as dissolved in a solvent. The solvent useful in this invention is volatile and is not particularly limited as long as it can stably dissolve the polymers and is safe to the skin. Examples of such solvents include water, ethanol, isopropyl alcohol (IPA) and the like. They are used singly or in combination. The amount of the solvent is modified depending on the properties of the polymer compounds, optional ingredients and forms of the preparation, and is generally from 30 to 99.99% by weight, and preferably from 60 to 95% by weight, based on the total weight of the composition.

The efficacy of the keratotic plug remover of this invention is enhanced when a pigment is further incorporated together with the mentioned polymers. The pigment is not particularly limited, and both organic and inorganic pigments can be used. Examples of the inorganic pigments are zinc oxide, titanium oxide, silica, alumina, barium sulfate, zirconium oxide, calcium carbonate, calcium silicate, ceramics, hydroxyapatite, boron nitride, sericite, mica, talc, kaolin, montmorillonite, hectorite, saponite, black iron oxide, yellow iron oxide, red iron oxide, prussian blue, ultramarine, carbon black, pearlescent pigments and so on. Examples of the organic pigments are silk powders, cellulose powders, poly(meth)acrylic ester resins, polyamide resins, polyolefin resins, polyimide resins, polyurethane resins, polyester resins, polyether resins, polyvinyl chloride resins, urea resins, polyformaldehyde resins, polycarbonate resins, polyvinylacetate resins, polyvinylidene chloride resins, polyacrylonitrile resins, polysulfone resins, polystyrene resins, polyurea resins, silicone resins, melamine resins, polytetrafluoroethylene resins, rake pigments and azo dyes.

The particle size of the pigments is from 0.001 to 1000 micrometers, and preferably from 0.01 to 500 micrometers. Particle size of less than 0.001 micrometer is not preferred because good dispersibiiity cannot be obtained. Particle size over 1000 micrometers is not preferred, either, because of an unfavorable, sensation to the skin. The mentioned pigments can be used as a complex or a mixture of one or more, if desired. The amount of the pigment is from 0.1 to 70% by weight, preferably from 1 to 40% by weight based on the total weight of the preparation.

When an oil component is further incorporated together with the polymers, the keratotic plug remover of this invention can achieve excellent removal of keratotic plugs without giving irritation to the skin. This is because the strength of the film at which it breaks upon peeling-off can be controlled by the oil component.

The oil component which is useful in this invention is a glycerol derivative represented by formula (I):



(I)

wherein one of Z^1 and Z^2 represents R^2-Y- and the other represents a hydroxyl group or R^3-Y-, and R^1, R^2 and R^3 independently represent a hydrocarbon group, the total carbon number of which ranges from 13 to 40, and the hydrocarbon group may or may not be substituted by a silicone residual group. X and Y independently represent an oxygen atom or a group -COO-, (a carboxyl group in which the C atom is bonded to R^1, R^2, or R^3). Other oily ingredients which are generally incorporated into cosmetic preparations can also be used. Examples of the oil component which is useful in this invention include vegetable oils such as avocado oil, tsubaki oil, macadamia nut oil, olive oil and jojoba oil; animal oils and fats such as beef tallow, lard and egg yolk fat; aliphatic acids such as oleic acid and isostearic acid; alcohols such as hexadecyl alcohol and oleyl alcohol; esters such as cetyl 2-ethylhexanoate, 2-ethylhexyl palmitate, 2-octyldodecyl myristate, neopentyl glycol di-2-ethyl hexanoate, 2-octyldodecyl oleate, isopropyl myristate, glycerol triisostearate, mono-2-ethylhexanoic glyceryl di-paramethoxycinnamate; and hydrocarbons such as dimethylpolysiloxane, dimethyl cyclopolysiloxane, methylphenyl polysiloxane, methylhydrogen polysiloxane, octamethyl cyclotetrasiloxane, octamethyl cyclopentasiloxane, decamethylcyclopentasiloxane, liquid paraffin, squalane, vaseline and solid paraffin.

Among these oil components, glycerol derivatives of formula (1) which are liquid at 20°C are preferred, and particularly, tri-2-ethylhexanoic glycerol, 1-isostearoyl-3-myristoyl glycerol, 2-ethylhexanoic diglyceride, 1-hexyl-3-undecamethylhexasiloxy propynyl glycerol are most preferred.

The amount of the oil components to be incorporated into the keratotic plug remover of this invention is from 0.5 to 30% by weight, preferably, 1 to 15% by weight based on the total weight of composition.

The keratotic plug remover preparation of this invention can further contain optional ingredients which are generally incorporated into cosmetic preparations. Examples of such optional ingredients include ethylene glycol, diethylene glycol, triethylene glycol and higher polyethylene glycols; propylene glycol, dipropylene glycol and higher polypropylene glycols, 1,3-butylene glycol, 1,4-butylene glycol and other butylene glycols; glycerol, diglycerol and higher polyglycerols; sugaralcohols such as sorbitol, mannitol, xylitol and maltitol; ethylene oxides (hereinafter referred to as EO) such as glycerols; addition products of propylene oxide (hereinafter referred to as PO); EO or PO adducts of sugaralcohols; monosaccharides such as galactose, glucose and fructose, and their EO or PO adducts; polysaccharides such as maltose and lactose, and their EO or PO adducts (polyols); surfactants such as POE alkyl ethers (POE is polyoxyethylene), POE branched alkyl ethers, POE sorbitan esters, POE glycerol fatty acid esters, POE hydrogenated castor oil, sorbitan ester, glycerol fatty acid esters and polyglycerol fatty acid ester; drugs such as vitamins, antiphlogistics, activators, UV absorbers and the like; water-swelling clay minerals such as montmorillonite, saponite and hectorite; polysaccharides such as carageenan, xanthangum, sodium alginate, pullulan, methylcellulose, carboxymethylcellulose, hydroxyethylcellulose and hydroxypropylcellulose; synthetic polymers such as carboxyvinyl polymers, polyvinyl pyrrolidones and polyvinyl alcohols. They are incorporated into the preparation of the present invention in such amounts that will not impede the effects of the invention. In particular, when polyols are used, they are preferably incorporated by 0.01 to 50% by weight based on the total preparation.

The keratotic plug remover according to this invention may take a form of a poultice using cotton cloth, rayon cloth, tetron cloth, nylon cloth, either woven or non-woven, or using a plastic film sheet, beside pack preparations.

The keratotic plug remover of this invention can be manufactured according to conventional processes for the manufacture of ordinary packs and poultice.

The manner of removing keratotic plugs by the use of the keratotic-plug remover of the invention is the same as the manner of using ordinary packs and poultice. Namely, when a pack preparation is used, it is first applied to the part of the skin which has keratotic plugs, particularly likely to the nose, chin and forehead, and after dried, it is peeled off.

Since the keratotic plug remover of this invention effectively removes keratotic plugs, the conspicuousness of the skin pores is mitigated, skin pores are maintained clean, and healthy skin can be obtained. Further, the remover of this invention does not hurt the skin.

Other features of the invention will become apparent in the course of the following descriptions of exemplary embodiments which are given for illustration of the invention and are not intended to be limiting thereof.

EXAMPLES

Where not otherwise indicated all amounts in the examples are in terms of % by weight based on the total weight of the composition.

Example 1:

Keratotic plug removers were prepared according to the pack preparation method mentioned below using the polymers listed in Table 1. A panel washed their face and used the preparation on their faces at an application rate of 0.1 ml/cm^2. The conditions of use were a temperature of 25°C, 50% humidity for 30 minutes. When 30 minutes had passed, the pack was peeled off. The ratio of removal of the keratotic plugs was calculated according to the following equation for evaluation.

$$\text{Removal ratio of keratotic plugs} = \frac{\text{number of keratotic plugs adhered on 1cm}^2\text{pack}}{\text{number of keratotic plugs existing in the 1 cm}^2\text{ wing skin of nose}} \times 100$$

The results are also shown in Table 1.

Evaluation:

A: over 20% removal ratio of keratotic plugs
B: 5 to 20% removal ratio of keratotic plugs
C: less than 5% removal ratio of keratotic plugs

Preparation:

Polymer	15 to 20% by weight
Glycerol	5
HCO60 (polyoxyethylene hydrogenated castor oil 60EO adduct)	1
Ethanol	5
Perfume	0.5
Antiseptic	suitable amount
Purified water	67.5 to 72.5
Total	100.0

Table 1

Polymers		Anionic/ Cationic	Evaluation (Removal of keratotic plugs)
IONIC	Poly 2-acrylamide-2-methylpropane sulfonate (AMPS) (MW: 500,000)	Anionic	A
	Polymethacryloyloxymethyl succinate (MW: 200,000)	Anionic	A
	Polymer of Na-styrene sulfonic acid (NaSS) (MW: 100,000)	Anionic	A
	Polymer of methacrylic acid (MAA) (MW: 200,000)	Anionic	A
	Copolymer of NaSS/MAA (1:1) (MW: 400,000)	Anionic	A
	Polymethacryloyloxyethyl trimethyl ammonium chloride (QUAT) (MW: 400,000)	Cationic	A
	Polymethacryloyloxyethyl triethyl ammonium diethyl sulfate (DEAMA-DES) (MW: 300,000)	Cationic	A
	Polymethacrylamidepropyl trimethyl ammonium chloride (MAPTAC)/polyacrylamidepropyl trimethyl ammonium chloride (DMAPAAm-Q) copolymer (8:2 by molar ratio) (MW:300,000)	Cationic	A
NONIONIC	Polyvinyl alcohol (PVA) (MW: 100,000)	-	C
	Polyethylene oxide (PEO) (MW: 1,000,000)	-	C
	Pullulan (MW: 70,000)	-	C
	Hydroxyethylcellulose (HEC) (MW: 100,000)	-	C
	Polyvinyl pyrrolidone (PVP) (MW: 600,000)	-	C

Example 2:

Keratotic plug removers were prepared using the polymers listed in Table 2, and the removal ratio of keratotic plugs

and the pain at the time of peeling-off were checked.

The polymers were individually prepared into an aqueous 20-30% by weight solution, and members of the panel used in the same manner as in Example 1.

Removal ratio of keratotic plugs:

See the equation in Example 1.

Evaluation:

(Removal ratio of keratotic plugs)

A: 35% or more
B: 20 to 34%
C: 5 to 19%
D: less than 5%

(Pain at the time of peeling-off)

slight pain: +
considerable pain: ++

Table 2

Polymers	Anionic/Cationic	Removal of Keratotic plugs	Pain upon peeling-off
Poly-2-acrylamide-2-methylpropane sulfonate (AMPS) (MW: 500,000)	Anionic	B	++
Polymethacryloyloxymethyl succinate (MW: 200,000)	Anionic	B	+
Polymer of Na · styrene sulfonic acid (NaSS) (MW: 100,000)	Anionic	A	++
Methacrylic acid (MAA) polymer (MW: 200,000)	Anionic	B	++
NaSS/MAA copolymer (1:1) (MW: 400,000)	Anionic	A	++
Polymethacryloyloxyethyl trimethylammonium chloride (QDM) (MW: 400,000)	Cationic	A	+
Polymethacrylamidepropyl trimethylammonium chloride (MAPTAC) (MW: 300,000)	Cationic	A	+
MAPTAC/polyacrylamidepropyl trimethyl ammonium chloride (DMAPAAm-Q) copolymer (8:2) (MW: 300,000)	Cationic	A	+
MAPTAC (MW: 300,000)/QDM (MW: 400,000) mixture	Cationic	A	+

Example 3:

Keratotic plug removers having the formulations as in Table 3 were prepared according to the conventional manner, and the keratotic plug removing performance was evaluated. The results are shown in Table 4.

Evaluation method:

Panel members washed their faces and applied keratotic plug removers onto their cheeks (0.1 ml/cm^2). The application was allowed to set at 25°C, humidity 50% for 30 minutes, and subsequently the pack film was peeled off. The number of the members who used an invention product A on their left cheek and an invention product B on their right cheek was the same as the number of the members who used an invention product B on their left cheek and an invention product A on their right cheek.

The panel members evaluated the removers by answering "Invention product A removed better", "Invention product A and Invention product B were almost the same concerning the removal performance" or "Invention product B removed better", and their percentages were obtained.

Table 3

Components (% by weight)	Invention products A			Invention products B	
	1	2	3	1	2
Poly-2-acrylamide-2-methylpropane sulfonate (AMPS) (MW: 500,000)	25	25	-	25	-
Polymethacryloyloxyethyltrimethyl ammonium chloride (QDM) (MW: 400,000)	-	-	25	-	25
Silica (av. particle size = 5 micrometers)	-	-	10	-	-
Zinc oxide (av. particle size: 0.04 micrometers)	3	-	-	-	-
Sericite (long axis: 5 to 10 micrometers)	-	10	-	-	-
HCO40 (Polyoxyethylene hydrogenated castor oil 40 EO adduct)	3	3	3	3	3
Glycerol	5	5	5	5	5
Perfume	0.5	0.5	0.5	0.5	0.5
Antiseptic	suitable amount				
Purified water	balance				

Table 4

Left (Right)	Right (Left)	Invention product A removed better	Invention products A and B are similar	Invention product B removed better
Invention product A1	Invention product B1	90	10	0
Invention product A2	Invention product B1	90	10	0
Invention product A3	Invention product B2	80	20	0

Example 4:

The keratotic plug removers as formulated in Table 5 were prepared according to the conventional manner.

The obtained keratotic plug removers were used by a panel consisting of 20 members as in the same manner described in Example 1. The pain upon peeling-off was evaluated with the criteria below. The results are shown in Table 5. Concerning the keratotic plug removal, all preparations removed well.

Evaluation:

○: No pain felt
X: Pain felt

Table 5

Components (% by weight)	Invention products C			Invention products D	
	1	2	3	1	2
Poly-2-acrylamide-2-methylpropane sulfonate (AMPS) (MW: 500,000)	25	25	-	25	-
Polymethacryloyloxyethyl triammonium chloride (QDH) (MW: 400,000)	-	-	25	-	25
Tri-2-ethyl hexanoic glycerol	3	-	3	-	-
2-Ethylhexanoic diglyceride	-	3	-	-	-
Glycerol	5	5	5	5	5
HCO40 (Polyoxyethylene hydrogenated castor oil 40 EO adduct)	1	1	1	1	1
Squalane	1	1	1	-	-
Ethanol	5	5	5	5	5
Perfume	0.5	0.5	0.5	0.5	0.5
Antiseptic	suitable amount				
Purified water	balance				
Pain when peeled off	O	O	O	X	X

Example 5:

The keratotic plug removers as formulated in Table 6 were prepared according to the conventional manner. The obtained keratotic plug removers removed keratotic plugs effectively without giving pains at the time of peeling off.

Table 6

Components (% by weight)	Invention products E												
	4	5	6	7	8	9	10	11	12	13			
Polymethacrylamidepropyl trimethylammonium chloride (MAPTAC) (MW: 500,000)									10	10			
Polymethacryloyloxyethyl trimethylammonium chloride (QDM) (MW: 400,000)							10	10					
Na-Styrene sulfonic acid / Methacrylic acid copolymer (MW: 400,000)	25												
Poly 2-acrylamide-2-methylpropane sulfonate (NAPS) (MW: 500,000)		30				20							
Polymethacrylamidepropyl trimethylammonium chloride (MAPTAC) (MW: 50,000)			35					20		20			
Polymethacryloyloxyethyl trimethylammonium chloride (QDM) (MW: 70,000)				30	20		20		20				
Polyvinyl alcohol (MW: 30,000)					5	5							
PEG 200 (polyethylene glycol 200)	5	5	5	5	3	3	3	3	3	3			
HCO 40 (Polyoxyethylene hydrogenated castor oil 40 EO adduct)	1	1	1	1	1	1	1	1	1	1			
Squalane	1	1	1	1	1	1	1	1	1	1			
2-ethylhexanoic diglyceride	3				2		3	3	3	3			
Tri-2-ethylhexanoic glycerol	1	2											
1-Hexyl-3-undecamethylhexasiloxane propynyl glycerol				3		2		2		2			
1-Isostearoyl-3-myristoylglycerol		2	3				3		3				
Silica			10	10									
Sericite	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5			
Perfume	← suitable amount →												
Antiseptic	← suitable amount →												
Water	← balance →												

Example 6:

A keratotic plug remover having the following formulation was prepared.

Polymethacryloyloxy trimethylammonium chloride (QDM) (MW: 400,000) Sorbitol	27.0 wt.% 3.0
Sericite	3.0
Ethanol	5.0
Antiseptic	suitable amount
Water	balance

Example 7:

A keratotic plug remover having the following formulation was prepared.

Polymethacryloyloxy trimethylammonium chloride (QDM) (MW: 250,000)	27.0 wt.%
Polyoxyethylene hydrogenated castor oil (E.O. 20)	2.0
Squalane	0.5
1-Isostearoyl-3-myristoyl glycerol (DGMI)	1.5
86% Glycerol	2.0
Propylene glycol	1.0
Sericite	3.0
Ethanol	5.0
Antiseptic	suitable amount
Water	balance

Example 8:

A keratotic plug remover having the following formulation was prepared.

Polymethacryloyloxy trimethylammonium chloride (QDM) (MW: 200,000)	15.0 wt.%
Polymethacrylamidepropyl trimethyl ammonium chloride (MAPTAC) (MW: 300,000)	15.0
Polyoxyethylene hydrogenated castor oil (E.O. 40)	1.5
Squalane	0.5
2-Ethylhexanoic triglyceride	2.0
Sorbitol	3.0
Kaolin	7.0
Titanium oxide	2.0
Ethanol	5.0
Antiseptic	suitable amount
Water	balance

Claims

Claims for the following Contracting States : DE, FR, GB

1. A keratotic plug remover composition, comprising a cationic polymer compound having a salt forming group, wherein said polymer is a synthetic cationic polymer selected from the group consisting of:

 (a) a cationic polymer of one or more cationic monomers;

 (b) a cationic copolymer containing units of an amphoteric monomer;

 (c) a cationic copolymer containing units of a monomer having no salt forming group; and

 (d) mixtures thereof

2. The keratotic plug remover composition of Claim 1, comprising a solvent being further incorporated thereinto.

3. The keratotic plug remover composition of Claim 1, comprising a pigment being further incorporated thereinto.

4. The keratotic plug remover composition of Claim 1, comprising an oil component being further incorporated thereinto.

5. The keratotic plug remover composition of Claim 1, comprising a solvent and an oil component being further incorporated thereinto.

6. The keratotic plug remover composition of Claim 1, comprising a solvent, an oil component and a pigment being further incorporated thereinto.

7. The keratotic plug remover composition of Claim 1, wherein said cationic monomer is selected from the group consisting of dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, dimethylaminopropyl acrylamide, dimethylaminopropyl methacrylamide, dimethylaminostyrene, dimethylaminomethylstyrene, 4-vinyl pyridine, 2-vinyl pyridine and quaternerized products thereof.

8. The keratotic plug remover composition of Claim 7, comprising a solvent being further incorporated thereinto.

9. The keratotic plug remover composition of Claim 7, comprising a pigment being further incorporated thereinto.

10. The keratotic plug remover composition of Claim 7, comprising an oil component being further incorporated there-

into.

11. The keratotic plug remover composition of Claim 7, comprising a solvent and an oil component being further incorporated thereinto.

12. The keratotic plug remover composition of Claim 7, comprising a solvent, an oil component and a pigment being further incorporated thereinto.

Claims for the following Contracting State : ES

1. Use of a synthetic cationic polymer selected from the group consisting of:

 (a) a cationic polymer of one or more cationic monomers;

 (b) a cationic copolymer containing units of an amphoteric monomer;

 (c) a cationic copolymer containing units of a monomer having no salt forming group; and

 (d) mixtures thereof,

 for the production of a keratotic plug remover composition, comprising a cationic polymer compound having a salt forming group.

2. The use of Claim 1, wherein said cationic monomer is selected from the group consisting of dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, dimethylaminopropyl acrylamide, dimethylaminopropyl methacrylamide, dimethylaminostyrene, dimethylaminomethylstyrene, 4-vinyl pyridine, 2-vinyl pyridine and quaternerized products thereof.

3. The use of any one of Claims 1 or 2, wherein the keratotic plug remover composition further comprises a solvent.

4. The use of any one of Claims 1 or 2, wherein the keratotic plug remover composition further comprises a pigment.

5. The use of any one of Claims 1 to 4, wherein the keratotic plug remover composition further comprises an oil component.

6. The use of Claim 5, comprising a solvent being further incorporated thereinto.

7. The use of Claim 6, comprising a pigment being further incorporated thereinto.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : DE, FR, GB

1. Entferner für keratöse Komedonen, umfassend eine kationische Polymerverbindung mit einer salzbildenden Gruppe, wobei das Polymere ein synthetisches kationisches Polymeres ist, das ausgewählt ist aus der Gruppe, bestehend aus:

 (a) einem kationischen Polymeren aus einem oder mehreren kationischen Monomeren;

 (b) einem kationischen Copolymeren, das Einheiten eines amphoteren Monomeren enthält;

 (c) einem kationischen Copolymeren, das Einheiten eines Monomeren ohne salzbildende Gruppe enthält; und

 (d) Gemischen davon.

2. Entferner für keratöse Komedonen nach Anspruch 1, dem ferner ein Lösungsmittel einverleibt ist.

3. Entferner für keratöse Komedonen nach Anspruch 1, dem ferner ein Pigment einverleibt ist.

4. Entferner für keratöse Komedonen nach Anspruch 1, dem ferner eine Ölkomponente einverleibt ist.

5. Entferner für keratöse Komedonen nach Anspruch 1, dem ferner ein Lösungsmittel und eine Ölkomponente einverleibt sind.

6. Entferner für keratöse Komedonen nach Anspruch 1, dem ferner ein Lösungsmittel, eine Ölkomponente und ein Pigment einverleibt sind.

7. Entferner für keratöse Komedonen nach Anspruch 1, wobei das kationische Monomere ausgewählt ist aus der Gruppe, bestehend aus Dimethylaminoethylacrylat, Dimethylaminoethylmethacrylat, Dimethylaminopropylacrylamid, Dimethylaminopropylmethacrylamid, Dimethylaminostyrol, Dimethylaminomethylstyrol, 4-Vinylpyridin, 2-Vinylpyridin und quaternisierten Produkten davon.

8. Entferner für keratöse Komedonen nach Anspruch 7, dem ferner ein Lösungsmittel einverleibt ist.

9. Entferner für keratöse Komedonen nach Anspruch 7, dem ferner ein Pigment einverleibt ist.

10. Entferner für keratöse Komedonen nach Anspruch 7, dem ferner eine Ölkomponente einverleibt ist.

11. Entferner für keratöse Komedonen nach Anspruch 7, dem ferner ein Lösungsmittel und eine Ölkomponente einverleibt sind.

12. Entferner für keratöse Komedonen nach Anspruch 7, dem ferner ein Lösungsmittel, eine Ölkomponente und ein Pigment einverleibt sind.

Patentansprüche für folgenden Vertragsstaat : ES

1. Verwendung eines synthetischen kationischen Polymeren, ausgewählt aus der Gruppe bestehend aus:

 (a) einem kationischen Polymeren aus einem oder mehreren kationischen Monomeren;

 (b) einem kationischen Copolymeren, das Einheiten eines amphoteren Monomeren enthält;

 (c) einem kationischen Copolymeren, das Einheiten eines Monomeren ohne salzbildende Gruppe enthält; und

 (d) Gemischen davon,

 zur Herstellung eines Entferners für keratöse Komedonen, der eine kationische Polymerverbindung umfaßt.

2. Verwendung nach Anspruch 1, wobei das kationische Monomere ausgewählt ist aus der Gruppe, bestehend aus Dimethylaminoethylacrylat, Dimethylaminoethylmethacrylat, Dimethylaminopropylacrylamid, Dimethylaminopropylmethacrylamid, Dimethylaminostyrol, Dimethylaminomethylstyrol, 4-Vinylpyridin, 2-Vinylpyridin und quaternisierte Produkte davon.

3. Verwendung nach einem der Ansprüche 1 oder 2, wobei der Entferner für keratöse Komedonen ferner ein Lösungsmittel umfaßt.

4. Verwendung nach einem der Ansprüche 1 oder 2, wobei der Entferner für keratöse Komedonen ferner ein Pigment umfaßt.

5. Verwendung nach einem der Ansprüche 1 bis 4, wobei der Entferner für keratöse Komedonen ferner eine Ölkomponente umfaßt.

6. Verwendung nach Anspruch 5, wobei dem Entferner ferner ein Lösungsmittel einverleibt ist.

7. Verwendung nach Anspruch 6, wobei dem Entferner ferner ein Pigment einverleibt ist.

Revendications

Revendications pour les Etats contractants suivants : DE, FR, GB

1. Composition pour l'élimination de bouchons kératotiques, comprenant un composé polymère cationique ayant un groupe formant sel, dans laquelle ledit polymère est un polymère cationique synthétique choisi dans le groupe constitué par :

 (a) un polymère cationique d'un ou plusieurs monomères cationiques ;
 (b) un copolymère cationique contenant des unités d'un monomère amphotère ;
 (c) un copolymère cationique contenant des unités d'un monomère n'ayant pas de groupe formant sel ; et
 (d) des mélanges de ceux-ci.

2. Composition pour l'élimination de bouchons kératotiques selon la revendication 1, comprenant un solvant qui y est en outre incorporé.

3. Composition pour l'élimination de bouchons kératotiques selon la revendication 1, comprenant un pigment qui y est en outre incorporé.

4. Composition pour l'élimination de bouchons kératotiques selon la revendication 1, comprenant un composant huileux qui y est en outre incorporé.

5. Composition pour l'élimination de bouchons kératotiques selon la revendication 1, comprenant un solvant et un composant huileux qui y sont en outre incorporés.

6. Composition pour l'élimination de bouchons kératotiques selon la revendication 1, comprenant un solvant, un composant huileux et un pigment qui y sont en outre incorporés.

7. Composition pour l'élimination de bouchons kératotiques selon la revendication 1, dans laquelle ledit monomère cationique est choisi dans le groupe constitué de l'acrylate de diméthylaminoéthyle, du méthacrylate de diméthylaminoéthyle, du diméthylaminopropyl acrylamide, du diméthylaminopropyl méthacrylamide, du diméthylaminostyrène, du diméthylaminométhylstyrène, de la 4-vinyl pyridine, de la 2-vinyl pyridine et des produits quaternisés de ceux-ci.

8. Composition pour l'élimination de bouchons kératotiques selon la revendication 7, comprenant un solvant qui y est en outre incorporé.

9. Composition pour l'élimination de bouchons kératotiques selon la revendication 7, comprenant un pigment qui y est en outre incorporé.

10. Composition pour l'élimination de bouchons kératotiques selon la revendication 7, comprenant un composant huileux qui y est en outre incorporé.

11. Composition pour l'élimination de bouchons kératotiques selon la revendication 7, comprenant un solvant et un composant huileux qui y sont en outre incorporés.

12. Composition pour l'élimination de bouchons kératotiques selon la revendication 7, comprenant un solvant, un composant huileux et un pigment qui y sont en outre incorporés.

Revendications pour l'Etat contractant suivant : ES

1. Utilisation d'un polymère cationique synthétique choisi dans le groupe constitué par :

 (a) un polymère cationique d'un ou plusieurs monomères cationiques ;
 (b) un copolymère cationique contenant des unités d'un monomère amphotère ;
 (c) un copolymère cationique contenant des unités d'un monomère n'ayant pas de groupe formant sel ; et
 (d) des mélanges de ceux-ci,

 pour la production d'une composition pour l'élimination de bouchons kératotiques, comprenant un composé

polymère cationique ayant un groupe formant sel.

2. Utilisation selon la revendication 1, dans laquelle ledit monomère cationique est choisi dans le groupe constitué de l'acrylate de diméthylaminoéthyle, du méthacrylate de diméthylaminoéthyle, du diméthylaminopropyl acrylamide, du diméthylaminopropyl méthacrylamide, du diméthylaminostyrène, du diméthylaminométhylstyrène, de la 4-vinyl pyridine, de la 2-vinyl pyridine et des produits quaternisés de ceux-ci.

3. Utilisation selon la revendication 1 ou 2, dans laquelle la composition pour l'élimination des bouchons kératotiques comprend en outre un solvant.

4. Utilisation selon la revendication 1 ou 2, dans laquelle la composition pour l'élimination de bouchons kératotiques comprend en outre un pigment.

5. Utilisation selon l'une quelconque des revendications 1 à 4, dans laquelle la composition pour l'élimination de bouchons kératotiques comprend en outre un composant huileux.

6. Utilisation selon la revendication 5, comprenant un solvant qui y est en outre mis en oeuvre.

7. Utilisation selon la revendication 6, comprenant un pigment qui y est en outre mis en oeuvre.

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EINGEGANGEN
14. MRZ. 1997
Erled. April 23.

Datum/Date
13/03/97

Zeichen/Ref /Réf	Anmeldung Nr./Application No./Demande n° //Patent Nr /Patent No /Brevet n°.
EA-8513	92108097.4-2114 0514760

Anmelder/Applicant/Demandeur//Patentinhaber/Proprietor/Titulaire
KAO CORPORATION

DECISION TO GRANT A EUROPEAN PATENT PURSUANT TO ARTICLE 97(2) EPC

Following examination of European patent application No. 92108097.4 a European patent with the title and the supporting documents indicated in the communication pursuant to Rule 51(4) EPC dated 06.09.96 is hereby granted in respect of the designated Contracting States. Any modifications which were subsequently requested have been approved by the Examining Division. Any corrections requested by the applicant a f t e r receipt of the communication under Rule 51(6) and received at the EPO on 00.00.00 have been taken into account.

Patent No. : 0514760
Date of filing : 13.05.92
Priority claimed : 15.05.91/ JP 110342/91
08.04.92/ JP 87032/92

Designated Contracting States and Proprietor(s) : DE-ES-FR-GB
KAO CORPORATION
1-14-10, Nihonbashikayaba-cho
Chuo-ku Tokyo/JP

This decision will take effect on the date on which the European Patent Bulletin mentions the grant (Art. 97(4) and (5) EPC).

The mention of the grant will be published in European Patent Bulletin 97/17 of 23.04.97.

Examining Division
TOULACIS C RAUTER A H WEBER G

Registered letter

PROF. DR. GÜNTER WÄCHTERSHÄUSER
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June 25, 1996

Re: European Patent Application
No.: 92 108 097.4
KAO CORPORATION
Our Ref.: EA-8513

Response to the Communication dated January 15, 1996

A new set of Claims 1 to 12 is filed as well as amended pages 1 and 2 of the description. It is requested that the new material is used in the further prosecution.

Claim 1 has been slightly clarified terminologically.

It is respectfully believed that with the documents now on file the application is in the appropriate form for being allowed. If this should not be the case, an informal interview is requested or, if necessary, formal oral proceedings.

Respectfully submitted,

Günter Wächtershäuser
Patent Attorney

Encl.:
New Claims 1 to 12, tripl.
Amended pages 1 and 2, tripl.

92 108 097.4-2114
Kao Corporation
Our Ref.: EA-8513

June 25, 1996

New Claims

1. A keratotic plug remover composition, comprising a cationic polymer compound having a salt forming group, wherein said polymer is a synthetic cationic polymer selected from the group consisting of:

(a) a cationic polymer of one or more cationic monomers;

(b) a cationic copolymer containing units of an amphoteric monomer;

(c) a cationic copolymer containing units of a monomer having no salt forming group; and

(d) mixtures thereof

2. The keratotic plug remover composition of Claim 1, comprising a solvent being further incorporated thereinto.

3. The keratotic plug remover composition of Claim 1, comprising a pigment being further incorporated thereinto.

4. The keratotic plug remover composition of Claim 1, comprising an oil component being further incorporated thereinto.

5. The keratotic plug remover composition of Claim 1, comprising a solvent and an oil component being further incorporated thereinto.

6. The keratotic plug remover composition of Claim 1, comprising a solvent, an oil component and a pigment being further incorporated thereinto.

7. The keratotic plug remover composition of Claim 1, wherein said cationic monomer is selected from the group consisting of dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, dimethylaminopropyl acrylamide, dimethylaminopropyl methacrylamide, dimethylaminostyrene, dimethylaminomethylstyrene, 4-vinyl pyridine, 2-vinyl pyridine and quaternerized products thereof.

8. The keratotic plug remover composition of Claim 7, comprising a solvent being further incorporated thereinto.

9. The keratotic plug remover composition of Claim 7, comprising a pigment being further incorporated thereinto.

10. The keratotic plug remover composition of Claim 7, comprising an oil component being further incorporated thereinto.

11. The keratotic plug remover composition of Claim 7, comprising a solvent and an oil component being further incorporated thereinto.

12. The keratotic plug remover composition of Claim 7, comprising a solvent, an oil component and a pigment being further incorporated thereinto.

No. 92 108 097.4
EA-8513

TITLE OF THE INVENTION

KERATOTIC PLUG REMOVER

BACKGROUND OF THE INVENTION

Field of the Invention:

The present invention relates to a keratotic plug remover which excellently removes keratotic plugs formed in the pores of the skin, and a method of removing keratotic plugs from the skin utilizing such a keratotic plug remover.

Discussion of the Background:

Having conspicuous pores in the skin is a serious skin problem, especially for women, and is mainly caused by keratotic plugs formed in the pores of the skin. Keratotic plugs are dead epidermal cells keratinized together with sebaceous matters and dirt which plug the pores of the skin. If proper treatment is not given, not only conspicuous pores but also various skin troubles result. Accordingly, removal of keratotic plugs is advisable in view of the health and beauty of the skin.

Ordinary face detergents, make-up removers, however, cannot sufficiently remove the keratotic plugs.

The use of various anionic or non-ionic polymers for skin treatment is known (EP-A-323 652; US-A-4,126,142; JP-A-55127312; JP-A-6335511; JP-A-6357508; GB-A-2 144 133).

Pack preparations, which are applied to the skin and peeled off after dried, and which generally contain an anionic or nonionic polymer such as polyvinyl alcohol and polyvinyl pyrrolidone as a major component of a film forming agent, are still not

sufficiently effective for removing dirt from the skin pores and especially for removing keratotic plugs.

Thus, there remains a need for a keratotic plug remover which can effectively remove keratotic plugs formed in the pores of the skin and a method of removing keratotic plugs from the skin utilizing such plug removers.

SUMMARY OF THE INVENTION

Accordingly, it is one object of the present invention to provide novel keratotic plug removers which effectively remove keratotic plugs from the skin.

It is another object of the present invention to provide a method for removing keratotic plugs from the skin which utilized such keratotic plug removers.

These and other objects are achieved by the keratotic plug remover of claim 1.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The salt forming group of the polymer which is useful in the present invention is not particularly limited as long as it can form a salt in the presence of an acid or a base, and anionic, cationic and amphoteric groups are suitable. Examples of the salt forming group are carboxyl, sulfonic acid group, sulfuric acid residual group ($-OSO_3H$), phosphoric acid

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FAX 089/2399-4465

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EINGE... NG
09.SEP 1996
Erled. Qu. 6

Application No./Patent No.	Ref.	Date
92108097.4-2114	EA-8513	06.09.96
Applicant/Proprietor: KAO CORPORATION		

Communication under Rule 51(4) EPC

You are hereby informed that the Examining Division intends to grant a European patent on the basis of the above application with the text and drawings as indicated below:

Designated state(s): DE ES FR GB

Description, page(s):		
3-13,15,17,19,20,22	as originally filed received on 25.06.1996	with letter of 25.06.1996 ✓
1,2		
14,16,18,21,23-25	received on 25.05.1993	with letter of 25.05.1993
Claim(s), No(s).:		
1-12	received on 25.06.1996	with letter of 25.06.1996 ✓

A copy of the relevant documents is enclosed.

The title of the invention in the three official languages of the European Patent Office, the international patent classification, the designated Contracting States and the registered name of the applicant are shown on the attached EPO Form 2056.

You are requested to state your approval of the text specified above **within four months** of this notificati n. Failure to do so will result in refusal of the application under Article 97(1) EPC, except as provided by Rule 51(5) EPC, second sentence.

The filing of a divisional application is only possible up to the approval of the text specified above (Rul 25 (1) EPC).
Concerning the possibilities of accelerated prosecution of European patent applications reference is made to OJ EPO 1995, 841.

Further information concerning the acceptability f amendments or the filing of a separate set of claims for one or more designated Contracting States that hav entered a reservation under Article 167(2)(a) EPC will be found in the Guidelines for Examination in the EPO, C-VI, 4.8 to 4.10 and C-VI, 15.1.2 to 15.1.4.

If the translation of the priority document(s), as required by Article 88 (1) EPC, or the declaration according to Rule 38 (4) EPC has not yet been filed, it is to be filed within the time limit mentioned in Rule 38 (4) EPC at the latest.

Registered letter

S. Hue
Formalities Officer
Tel.No.: (089) 2399-8141

Enclosures: EPO Form 2056
Copies of the relevant documents

Registered letter

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November 16, 1995

Re: European Patent Application
No.: 92 108 097.4
KAO CORPORATION
Our Ref.: EA-8513

Response to the Communication dated May 10, 1995

Enclosed herewith is a new set of claims 1 to 12 and it is requested, that these claims are used in the further procecution. Claim 1 has been clarified. Support for this amendment is found in the description at page 5, lines 12 to 17.

It is respectfully submitted, that polyvinyl pyrrolidone mentioned in D6 is not a cationic polymer. Rather, as shown in the enclosed copy of "Die Angewandte Makromolekulare Chemie 181 (1990), pages 93 to 101, poly(vinyl pyrrolidone)(PVP) is catalogized as a non-ionic homopolymer.

The discussion relating to document D6 in our previous letter may have been misinterpreted. The intention was to express that this reference gives no description or suggestion of the possibility that anyone of said first and second agent contain a cationic polymer.

It is therefore respectfully submitted, that the presently claimed subject matter is novel and inventive over all of the cited prior art references.

In case that the Examiner should still have doubts in this respect, an informal interview is requested or, if necessary, formal oral proceedings. The description will be adapted as soon as the allowable wording of the claims is known.

Respectfully submitted,

Günter Wächtershäuser

Patent Attorney

Encl.:
New claims
"Die Angewandte Markomolekulare Chemie 181"

Die Angewandte Makromolekulare Chemie 181 *(1990) 93–101 (Nr. 3042)*

Department of Chemistry, University of Delhi,
Delhi-110007, India

Study of multicomponent complexes between polycarboxylic acid, transition metal ions and non-ionic polymers

S. K. Chatterjee, A. M. Khan, Sudipta Ghosh, and D. Yadav

(Received 19 September 1989)

SUMMARY:

Multicomponent complexes of a typical polyelectrolyte like poly(acrylic acid) (PAA) have been prepared by incorporating transition metal ions (e. g. Cu(II) and Ni(II)) and non-ionic polymers (e. g. PVP, PEO) in the polyelectrolyte chain in a definite sequence. The formation of these complexes has been studied by several techniques, such as viscometry, potentiometry, conductometry, and IR spectroscopy. A scheme is suggested to explain the mode of formation of such complexes.

ZUSAMMENFASSUNG:

Mehrkomponentige Komplexe eines typischen Polyelektrolyten wie Polyacrylsäure (PAA) mit nichtionogenen Polymeren (PVP and PEO) und Übergangsmetallionen (Cu(II) und NI(II)) wurden hergestellt und mittels Viskosimetrie, Potentiometrie, Leitfähigkeitsmessungen und IR-Spektroskopie untersucht. Ein Schema, welches die Bildung dieser Komplexe erklärt, wird vorgeschlagen.

Introduction

The interaction of transition metal ions with polyelectrolytes has been widely studied by numerous methods[1,2]. Among polycarboxylic acids, the most extensively investigated are poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA). These polycarboxylic acids are also known to form interpolymer complexes with non-ionic homopolymers, such as poly(vinyl pyrrolidone) (PVP), poly(ethylene oxide) (PEO) etc., through hydrogen bonding and ion-dipole interactions[3–6]. Therefore, it was considered to be of interest to see whether both transition metal ions (e. g. Cu(II), Ni(II) etc.) as well as non-ionic homopolymer chains (e. g. PVP, PEO etc.) could be incorporated alternatively

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in the same polycarboxylic acid chain. When a part of the polycarboxylic acid chain is complexed with say, PVP, presumably it may lead to a twisting of the backbone of the polymer chain, and to counter balance the strain thus produced, PVP units are likely to be held at greater distance[2]. This is also likely to influence the Cu(II)-Cu(II) distance in polycarboxylic acid chains as well as the geometry of the polymer-metal complex. In the present investigation, transition metal ions (e.g. Cu(II) and Ni(II)) and non-ionic homopolymers (e.g. PVP and PEO) have been incorporated in the PAA chain in a definite sequence, and its effect has been studied through several experimental techniques, such as viscometry, potentiometry, conductometry, and IR spectroscopy. Efforts have been made to interpret formation of multicomponent complexes through structural characteristics of the polymers and the nature of the transition metal ions.

Experimental

Materials

Poly(acrylic acid) (PAA): Purified acrylic acid (distilled twice in vacuo, b.p. 63 °C/16 hPa) was polymerized with benzoyl peroxide as an initiator in a moist dioxane-methanol mixture[7] for 2.5 h in nitrogen atmosphere at 50 °C. The reaction mixture was dissolved in methanol and reprecipitated twice with ethyl acetate. The polymer was dried to constant weight in vacuo at 110 °C. The molecular weight of the polymer was calculated from viscosity data[7]. The weight average molecular weight was $\bar{M}_w = 4.0 \cdot 10^5$.

Poly(vinyl pyrrolidone) (PVP) was supplied by Fluka, USA. The $\bar{M}_w$ of the polymer was calculated[8] from viscosity data and found to be $2.4 \cdot 10^4$.

Poly(ethylene oxide) (PEO) was supplied by Iwai Kagaru Co., Japan, and its weight average molecular weight ($\bar{M}_w$) was found to be $1.9 \cdot 10^4$ as calculated[9] from viscosity data.

A dimethyl formamide-methanol mixture (v/v = 1/1) was used as solvent for all experimental measurements. The solvents were of analytical grade.

Characterizations

Conductometric titrations were carried out with a Leeds and Northrup (4959) conductance bridge[10]. The conductance of the mixed solutions was measured at various unit mole (um) ratios and the reproducibility of the values was found to be within ±2%.

pH-titrations were carried out with an EC digital pH meter (model pH 5651) using a combination electrode[10]. The concentration of the polymer solution was of the same order as in the conductance experiment (e.g. $5 \cdot 10^{-3}$ um/l).

The viscosity of the mixed solutions of the polymer, PVP, PEO and metal ions at various unit mole ratios was determined at 30 °C + 0.05 by an Ubbelohde viscometer for which the kinetic energy correction was negligible.

Results and discussion

The interaction of polyacrylic acid (PAA) with transition metal ions and non-ionic homopolymers has been studied in non-aqueous media. A 1:1 mixture of methanol and DMF has been found to be the most suitable medium for resolution of different stages of interaction. Fig. 1 shows the variation of conductance, apparent pH and reduced viscosity (η_{sp}/c) of 1 unit mole (um) of PAA solution on the successive addition of 0.2 um of PVP, 0.3 mol of Ni(II), 0.2 um of PVP and 0.3 mol of Ni(II), respectively. The non-ionic polymer and the transition metal ions have been added to PAA in the above sequence and in small instalments. Both the pH and the conductance curves (cf. curve C and

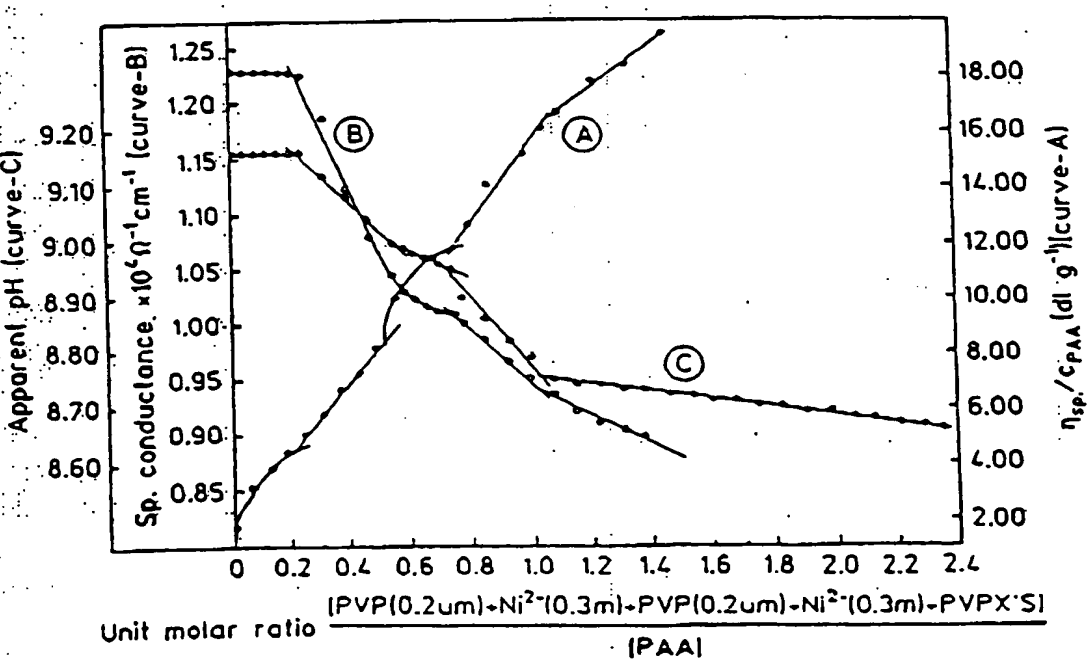


Fig. 1. Variation of reduced viscosity (A), conductance (B), and apparent pH (C) with unit mole ratio for polyacrylic acid-transition metal ion-non-ionic polymer system.

B of Fig. 1) show distinct steps and are identical in nature. Up to the addition of PVP (i.e. 0.2 um), both the conductance and apparent pH remained almost constant. In a medium of low dielectric constant, the carboxylic groups of PAA are expected to be mostly in unionized state, and this is likely to favour complex formation with PVP through hydrogen bonding[3]. However, these interactions may not change the concentration of hydrogen ions or other charged species in the solution. Thus a constant pH or conductance during this stage of complex formation could be anticipated. However, an abrupt fall in apparent pH as well as conductance was observed during the addition of 0.3 mol of Ni(II) ions. It is known that when transition metal ions interact with carboxylic groups, deprotonation takes place and H^+ ions are released[11, 12]. This can be attributed to the sharp fall in pH during this stage of interaction. However, the corresponding fall in conductance may be due to association of charged species in the medium of low dielectric constant. Subsequently, when 0.2 um of PVP was added, the pH and conductance continued to fall though at a much slower rate. An abrupt fall in pH and conductance was once again observed during the subsequent addition of 0.3 mol of Ni^{2+}.

One of the most interesting aspects of the reduced viscosity curves is the continuous increase in reduced viscosity observed when the component polymer and the metal ions were added to PAA in the above sequence. It is known that when metal ions interact with polyelectrolyte chains in aqueous medium, a sharp fall in viscosity is normally observed[12]. This is attributed to tightly coiled conformation acquired by metal complex of the polyelectrolyte. However, the contrasting behaviour which is observed in non-aqueous medium, perhaps may be due to a change in the degree of solvation of the complex, association of charged species in low dielectric constant medium, or trapped solvent molecules in the coiled structure of the complex. All these factors are likely to influence the reduced viscosity during complex formation.

In order to get more authentic evidence of these multicomponent complex systems, two non-ionic homopolymers (e.g. PVP and PEO) and two different transition metal ions (e.g. Ni(II) and Cu(II)) were added in specific sequences to PAA solution in non-aqueous medium (e.g. 1:1 mixture of DMF and methanol). The variation of apparent pH, conductance, reduced viscosity as well as specific sequences of addition of components are shown in Fig. 2 to 4.

On comparing Fig. 1 to 4, it can be seen that instead of adding Ni(II), if Cu(II) is added at the second stage of interaction, the fall in apparent pH and conductance is more abrupt, and during subsequent addition of non-ionic polymer, pH and conductance remain almost constant (compare Fig. 1 and 2 with Fig. 3 and 4). This obviously indicates that the nature and geometry of

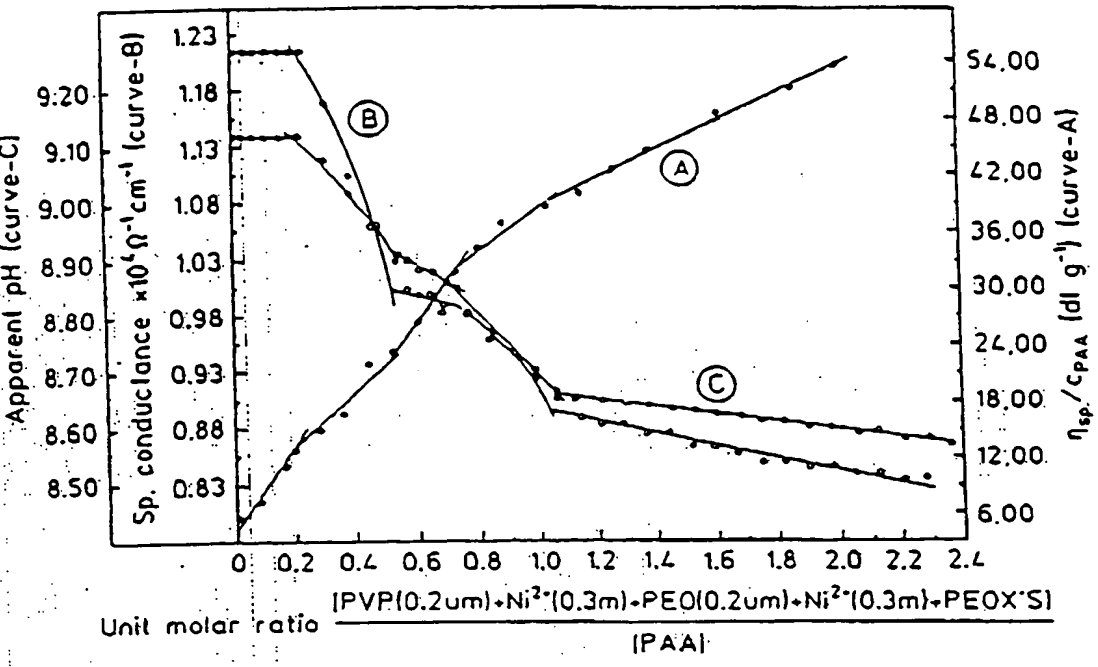


Fig. 2. Variation of reduced viscosity (A), conductance (B), and apparent pH (C) with unit mole ratio for polyacrylic acid-Ni^{2+}-PEO system.

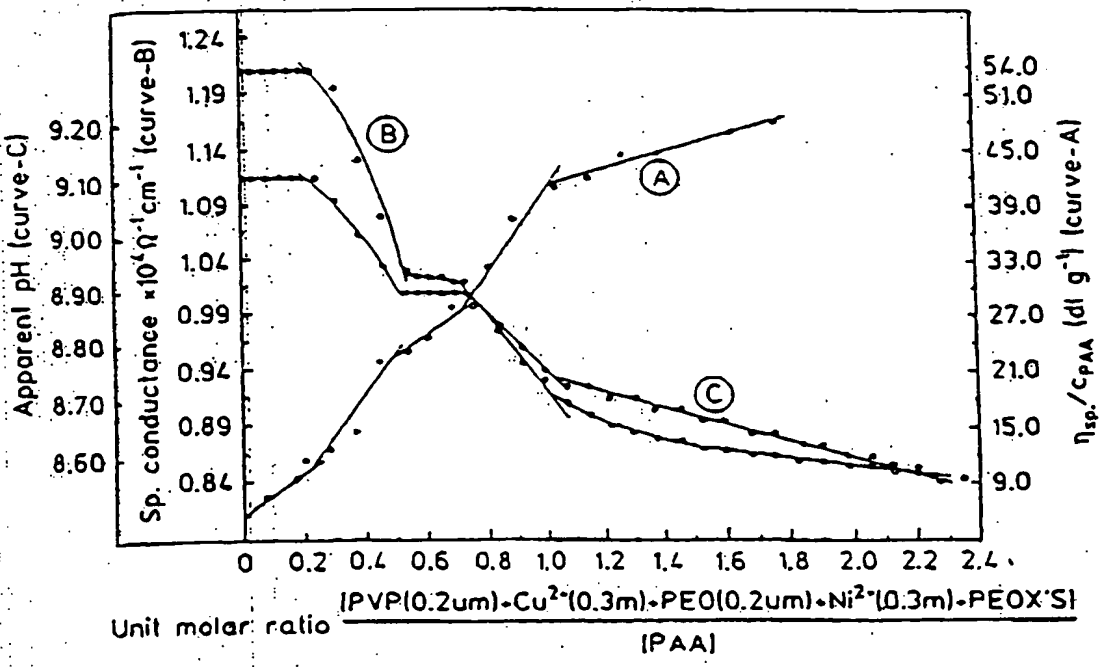
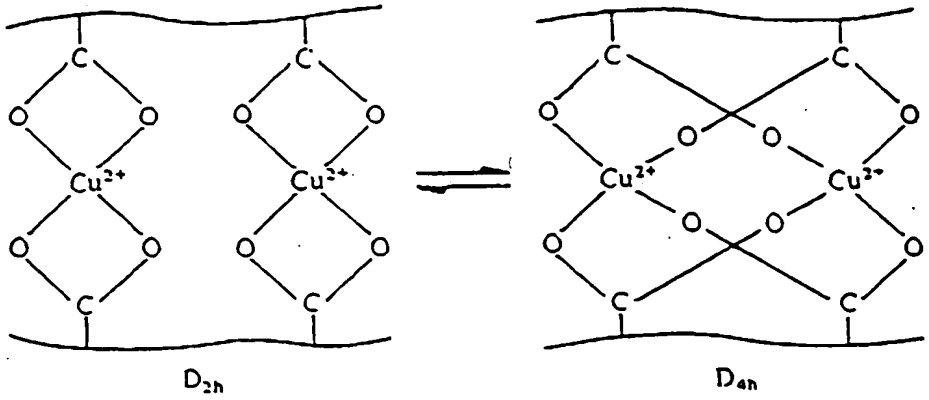


Fig. 3. Variation of reduced viscosity (A), conductance (B), and apparent pH (C) with unit mole ratio for polyacrylic acid-transition metal ions-PEO system.

complexes formed between Cu(II) and Ni(II) with PAA are different. Cu(II) is known to bind with PAA to form D_{4h} and D_{2h} type complexes as shown below[9]:



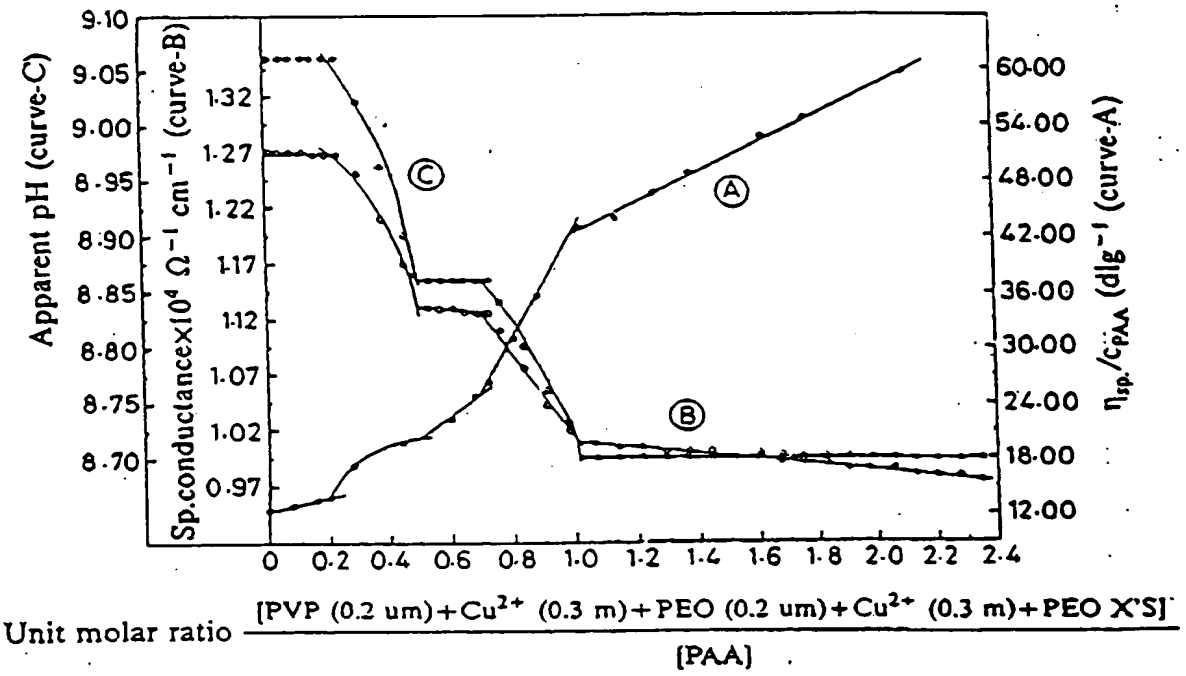
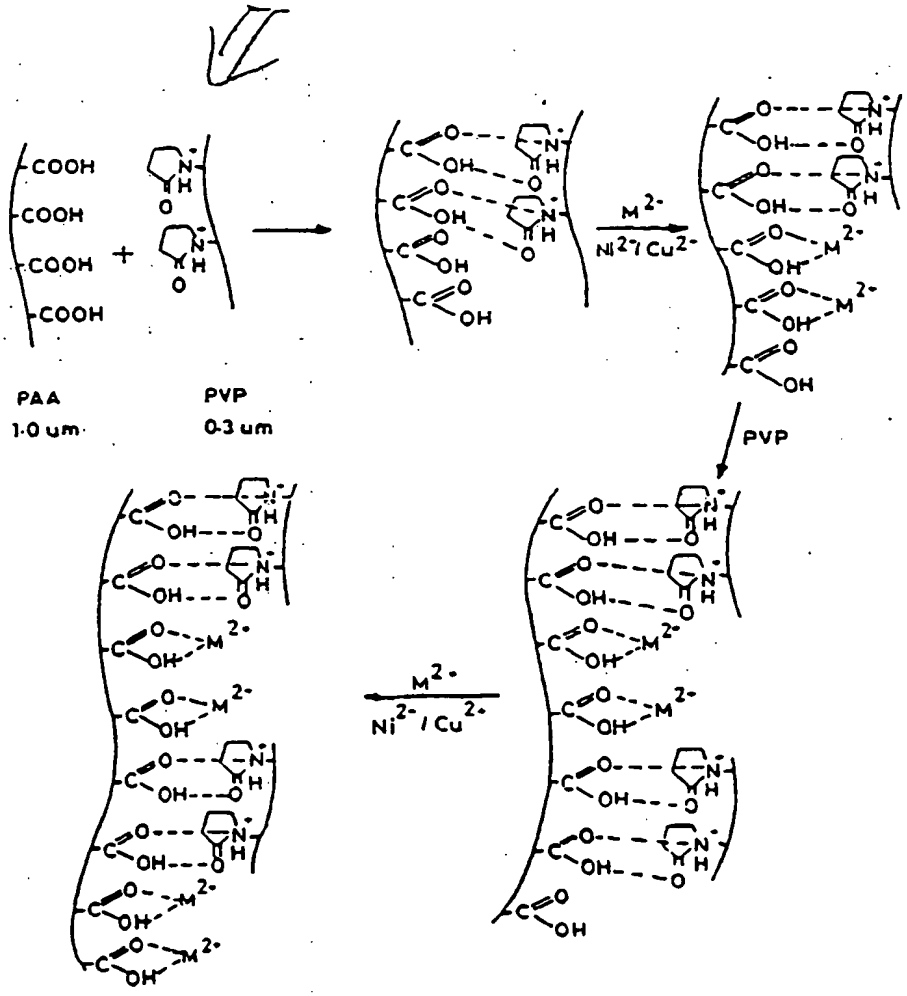


Fig. 4. Variation of reduced viscosity (A), conductance (B), and apparent pH (C) with unit mole ratio for PAA-Cu^{2+}-PEO system.

It is known that the equilibrium existing between D_{2h} and D_{4h} type symmetry is shifted more towards D_{2h} type in the presence of PVP[2]. In other words, in the presence of PVP, the Cu(II)-Cu(II) distance in the polyelectrolyte chain is increased which ultimately leads to the formation of D_{2h} type complex[2].

Morcellet[1] also studied the thermodynamic parameters of polycarboxylic acid-bivalent metal complexes, and found that Cu(II)-PAA complexes had large and positive entropy change and were predominantly endothermic, and consequently lowering of free energy (ΔG) for Cu(II) complexes was greater. Compared to this, Ni(II)-polycarboxylic acid complexes had lower positive entropy change and were less endothermic in character. Therefore, it was concluded that Cu(II) forms a comparatively more stable complex with polycarboxylic acid compared to other bivalent metal ions including Ni(II)[7]. It is evident from these arguments that the sequence distributions of Cu(II) and Ni(II) ions in the polyelectrolyte chains (e.g. PAA) are likely to be different, and this may possibly influence the geometry of the complexes as well.

On the basis of experimental observations and arguments based on them, the following scheme may be suggested for the formation of multicomponent interpolymer complexes involving polycarboxylic acid, metal ions and non-ionic polymers:



Tab. 1. IR spectral data of pure components (PAA, PVP) and the multicomponent complexes between them and metal ions.

Component/multicomponent complex	$\nu_{O-H_{str.}}$ (cm^{-1})	$\nu_{C=O_{str.}}$ (cm^{-1})
PAA	2980	1730
PVP	3270	1660
Complex (I) 1 um[a] PAA + 0.2 um PVP	3431	1685
Complex (II) 1 um PAA + 0.2 um PVP + 0.3 mol Cu^{2+}	3431	1685
Complex (III) 1 um PAA + 0.2 um PVP + 0.3 mol Cu^{2+} + 0.2 um PEO	3455	1669
Complex (IV) 1 um PAA + 0.2 um PVP + 0.3 mol Cu^{2+} + 0.2 um PEO + 0.3 mol Cu^{2+}	3437	1685

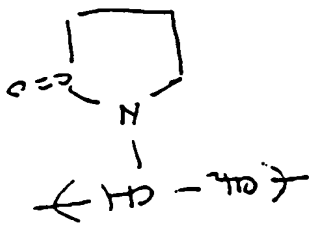
[a] um = unit mole.

The IR spectra of the complexes were recorded in KBr and compared with those of the pure components (i. e. PAA and PVP). Some of the spectral data are given in Tab. 1.

It is evident from the spectral data (cf. Tab. 1) that all complexes show a distinct shift in ν_{O-H} stretching and $\nu_{C=O}$ carbonyl frequencies, when compared to the pure components. However, incorporation of metal ions (e. g. Cu(II) or Ni(II)) to PAA-PVP complex did not bring about further shifts in the frequencies, though introduction of another non-ionic polymer (e. g. PEO) shifted the ν_{O-H} stretching frequency to a slightly higher value and the $\nu_{C=O}$ frequency to a little lower value (cf. Tab. 1). Obviously, the involvement of various functional groups of the component polymers during complex formation is quite evident from the spectral data.

In conclusion, it can be said that multicomponent complexes can be formed from a typical polyelectrolyte like polyacrylic acid (PAA), by incorporating non-ionic polymers (e. g. PVP and PEO) and transition metal ions (e. g. Cu(II) or Ni(II)) in the polyelectrolyte chain in a definite sequence. Such intermacromolecular complexes with coordinated metal ions are expected to affect the development of new polymer catalysts, redox systems, and membranes with selective permeability[14].

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92 108 097.4-2114
Kao Corporation
Our Ref.: EA-8513

November 16, 1995

New Claims

1. A keratotic plug remover composition, comprising a cationic polymer compound having a salt forming group, wherein said polymer is a synthetic cationic polymer selected from the group consisting of:

(a) a cationic polymer of one or more cationic monomers;

(b) a cationic copolymer between the cationic polymer (a) and an amphoteric monomer;

(c) a cationic copolymer between the cationic polymer (a) and a monomer having no salt forming group; and

(d) mixtures thereof

2. The keratotic plug remover composition of Claim 1, comprising a solvent being further incorporated thereinto.

3. The keratotic plug remover composition of Claim 1, comprising a pigment being further incorporated thereinto.

4. The keratotic plug remover composition of Claim 1, comprising an oil component being further incorporated thereinto.

5. The keratotic plug remover composition of Claim 1, comprising a solvent and an oil component being further incorporated thereinto.

6. The keratotic plug remover composition of Claim 1, comprising a solvent, an oil component and a pigment being further incorporated thereinto.

7. The keratotic plug remover composition of Claim 1, wherein said cationic monomer is selected from the group consisting of dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, dimethylaminopropyl acrylamide, dimethylaminopropyl methacrylamide, dimethylaminostyrene, dimethylaminomethylstyrene, 4-vinyl pyridine, 2-vinyl pyridine and quaternerized products thereof.

8. The keratotic plug remover composition of Claim 7, comprising a solvent being further incorporated thereinto.

9. The keratotic plug remover composition of Claim 7, comprising a pigment being further incorporated thereinto.

10. The keratotic plug remover composition of Claim 7, comprising an oil component being further incorporated thereinto.

11. The keratotic plug remover composition of Claim 7, comprising a solvent and an oil component being further incorporated thereinto.

12. The keratotic plug remover composition of Claim 7, comprising a solvent, an oil component and a pigment being further incorporated thereinto.

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Telephone numbers:

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Formalities officer (Formalities including extension of time limits) (0 89) 23 99- 8141

Assistant (other matters) (0 89) 23 99- 8141

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Patentanwalt,
Tal 29
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REPUBLIQUE FEDERALE D'ALLEMAGNE

Application No./Patent No.	Ref.	Date
92108097.4-2114	EA-8513	15.01.96
Applicant/Proprietor: KAO CORPORATION		

Communication pursuant to Article 96(2) and Rule 51(2) EPC

The /further/ examination of the above-identified application has revealed that it does not meet the requirements of the European Patent Convention for the reasons enclosed herewith. If the deficiencies indicated are not rectified the application may be refused pursuant to Article 97(1) EPC.

You are invited to file your observations and insofar as the deficiencies are such as to be rectifiable to correct the indicated deficiencies within a **period**

of 4 **months**

from the notification of this communication, this period being computed in accordance with Rules 78(3) and 83(2) and (4) EPC.

Amendments to the description, claims and drawings are to be filed where appropriate within the said period in **three copies** on separate sheets (Rule 36(1) EPC).

Failure to comply with this invitation in due time will result in the application being deemed to be withdrawn (Article 96(3) EPC).

EUROPÄISCHES PATENTAMT · EUROPEAN PATENT OFFICE · OFFICE EUROPÉEN DES BREVETS MÜNCHEN

G. Weber
Primary examiner
for the Examining Division

Enclosures: 1 page/s reasons (Form 2906)

Registered letter

The examination is being carried out on the following application documents:

Description:
Pages 1 to 22 as originally filed

Claims:
Nos. 1 to 12 filed with your letter of 16/11/95

The subject-matter of the amended claims is considered as being allowable (Articles 123(2), 54 and 56 EPC). Accordingly, You are requested to bring the description into line with the amended set of claims (Article 84 EPC).

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Europäisches Patentamt	European Patent Office	Office européen des brevets
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Application No./Patent No.	Ref.	Date
92108097.4-2114	EA-8513	10. 05. 95
Applicant/Proprietor: KAO CORPORATION		

Communication pursuant to Article 96(2) and Rule 51(2) EPC

The /further/ examination of the above-identified application has revealed that it does not meet the requirements of the European Patent Convention for the reasons enclosed herewith. If the deficiencies indicated are not rectified the application may be refused pursuant to Article 97(1) EPC.

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MÜNCHEN

G. Weber
Primary examiner
for the Examining Division

Enclosures: 1 page/s reasons (Form 2906)

Registered letter

The examination is being carried out on the following application documents:

Description:
Pages 1 to 25 as originally filed

Claims:
Nos. 1 to 12 filed with your letter of 18/04/95

1). The application in its amended form meets the requirements according to Article 123 (2) EPC.

2). Having regard to the prior art and to Your arguments submitted with letter of reply dated 18.04.95 the subject-matter of the amended claim 1 can still not be regarded as being novel (Articles 52(1) and 54 EPC).

JP-A-63-57508 (D6, according to Your numbering) considered in the form of its patent abstract of japan discloses the use of at least one cationic polymer as claimed.
In connection with this, it has to be stated that the wording of the amended claim 1 does not require that all polymers are cationic (see also Your letter of reply of 18.04.95 page 2, the fifth paragraph).

3). If the Applicant wishes to have an interview You are invited to contact the Examiner.

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Professional
Representative
before the European
Patent Office

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Erhardtstr. 27
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April 18, 1995

Re: European Patent Application
No.: 92 108 097.4-2114
Kao Corporation
Our Ref.: EA-8513

Response to the Communication dated October 10, 1994

Enclosed herewith is a new set of Claims 1 to 12. It is requested that the new claims are used in the further prosecution.

The features of new Claim 1 are duly supported by the original documents in original Claims 1 and 2 at the description, page 3, lines 17 to 26 and page 5, lines 12 to 17.

The subject matter now claimed is novel. None of the prior art references discloses a keratotic plug remover composition having the features defined in present Claim 1. Notably, there is no description in any of the citations of a composition which may be used as a keratotic plug remover and which contains a synthetic cationic polymer having a salt forming group.

D1 discloses the use of polyvinyl alcohol for preparing the cosmetic composition. However, the present composition is not relevant to such a nonionic polymer. In the present invention, polyvinyl alcohol is excluded, as described at the paragraph bridging between pages 1 and 2 of the present specification.

D2 discloses a polymerizable adhesive composition useful for the treatment of human skin for the removal of materials from the surface and sebaceous follicles. In particular, the polymerizable adhesive composition is disclosed as being alpha cyano-

acrylate. However, polymerized alpha cyanoacrylate is not a cationic polymer. In contrast, the newly claimed composition is always related to a cationic polymer.

D3 discloses a two-stage skin treating technique in which a film of sodium polystyrene sulfonate is applied to the skin and allowed to dry. However, this reference contains no disclosure or suggestion of keratotic plug remover compositions which contain a cationic polymer. Note that styrene sulfonic acid is disclosed as an anionic monomer on page 4, line 5 of the present specification.

D4 discloses a pack cosmetic composition consisting of two components. Of the components, the first component is described to contain polymers, e.g., sodium or potassium alginate and sodium polyacrylate. However, these polymers are not cationic polymers. In particular, sodium alginate is described as a natural origin or semi-synthesized polymers on page 3, line 13 of the present specification. In this point, the new Claim 1 explicitly defines the intended polymer as a synthetic polymer, not origin or semi-synthesized polymer.

D5 also discloses a pack cosmetic composition of two components, whose 1st component and 2nd component contain carboxy-modified polyvinyl alcohol and sodium or potassium salt of alginic acid, respectively. These polymers are all not cationic polymers, and again, sodium salt of alginic acid is not a synthetic polymer.

D6 discloses a film forming cosmetic pack composition associated with a combination of its first agent and second agent including polymer. However, this reference gives no description or suggestion of the possibility that both agents contain a cationic polymer.

D7 describes cosmetic compositions containing a copolymer of (meth)acrylic acid, an alkyl (meth)acrylate and an allyl derivative. No cationic polymers are described in D7.

D8 relates to aqueous gels based on hyaluronic acid and desoxyribonucleic acid usable in cosmetics. No synthetic polymers are described in D8, let alone a synthetic polymer as defined in Claim 1 of the present application.

Thus, in summary, none of the prior art references D1 to D8 destroys the novelty of the present invention.

Turning now to the inventive merit of the present invention, it is submitted that the compositions of the present invention as defined in new Claim 1 have the specific feature that they always contain a synthetic polymer having structural units of at least one type of cationic monomer. This type of composition is surprisingly more effective as a keratotic plug remover than similar compositions having anionic polymers or amphoteric polymers. Table 2 of the present specification compares compositions comprising anionic polymers with those comprising cationic polymers. There is clear evidence in Table 2 that the compositions of the present invention which contain cationic polymers are capable of exhibiting good performances in keratotic plug removal and low pain, compared with the other polymers.

Such effect as demonstrated by the Comparative Data in Table 2 is not predictable on the basis of the prior art because none of the prior art references contains any disclosure of compositions comprising a cationic polymer having a salt forming group. It is therefore respectfully submitted that the new claims, which are directed to originally disclosed preferred embodiments, are patentable over the cited prior art. In case that the Examiner should still have doubts in this respect, an informal interview is requested or, if necessary, formal oral proceedings. Any necessary amendment of the description including an adaption to the wording of the claims is postponed, until an allowable wording of the claims is known.

Respectfully submitted,

Günter Wächtershäuser
Patent Attorney

Enclosures
New Claims 1 to 12, tripl.

New Claims

1. A keratotic plug remover composition, comprising a polymer compound having a salt forming group, wherein said polymer is a synthetic polymer selected from the group consisting of:

(a) a polymer of one or more cationic monomers;

(b) a copolymer between the polymer (a) and an amphoteric monomer;

(c) a copolymer between the polymer (a) and a monomer having no salt forming group; and

(d) mixtures thereof.

2. The keratotic plug remover composition of Claim 1, comprising a solvent being further incorporated thereinto.

3. The keratotic plug remover composition of Claim 1, comprising a pigment being further incorporated thereinto.

4. The keratotic plug remover composition of Claim 1, comprising an oil component being further incorporated thereinto.

5. The keratotic plug remover composition of Claim 1, comprising a solvent and an oil component being further incorporated thereinto.

6. The keratotic plug remover composition of Claim 1, comprising a solvent, an oil component and a pigment being further incorporated thereinto.

7. The keratotic plug remover composition of Claim 1, wherein said cationic monomer is selected from the group consisting of dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, dimethylaminopropyl acrylamide, dimethylaminopropyl methacrylamide, dimethylaminostyrene, dimethylaminomethylstyrene, 4-vinyl pyridine, 2-vinyl pyridine and quaternerized products thereof.

8. The keratotic plug remover composition of Claim 7, comprising a solvent being further incorporated thereinto.

9. The keratotic plug remover composition of Claim 7, comprising a pigment being further incorporated thereinto.

10. The keratotic plug remover composition of Claim 7, comprising an oil component being further incorporated thereinto.

11. The keratotic plug remover composition of Claim 7, comprising a solvent and an oil component being further incorporated thereinto.

12. The keratotic plug remover composition of Claim 7, comprising a solvent, an oil component and a pigment being further incorporated thereinto.

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Erled. 4/14 FS 95/mk

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Assistant (other matters)	(0 89) 23 99- 8141

Application No./Patent No.	Ref.	Date
92108097.4-2114	EA-8513	04. 10. 94
Applicant/Proprietor: KAO CORPORATION		

Communication pursuant to Article 96(2) and Rule 51(2) EPC

The /further/ examination of the above-identified application has revealed that it does not meet the requirements of the European Patent Convention for the reasons enclosed herewith. If the deficiencies indicated are not rectified the application may be refused pursuant to Article 97(1) EPC.

You are invited to file your observations and insofar as the deficiencies are such as to be rectifiable to correct the indicated deficiencies within a **period**

of 4 **months**

from the notification of this communication, this period being computed in accordance with Rules 78(3) and 83(2) and (4) EPC.

Amendments to the description, claims and drawings are to be filed where appropriate within the said period in **three copies** on separate sheets (Rule 36(1) EPC).

Failure to comply with this invitation in due time will result in the application being deemed to be withdrawn (Article 96(3) EPC).

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G. Weber
Primary examiner
for the Examining Division

Enclosures: 3 page/s reasons (Form 2906)

Registered letter

The examination is being carried out on the following application documents:

Description:
Pages 1 to 13,15,17,19,20,22 as originally filed
Pages 14,16,18,21,23,24,25 as filed with your letter of 25.05.93

Claims:
Nos. 1 to 18 as originally filed
Nos. xx to xx filed with your letter of xx/xx/xx

1). The various definitions of the invention given in independent claims 1,6,8,10,12,14,16,17 and 18 are such that the claims as a whole are not clear and concise, contrary to Article 84 EPC. The claims should be recast to include only the minimum necessary number of independent claims in any one category, Rule 29(2) EPC, with dependent claims as appropriate, Rule 29(4) EPC.

.In the present case it is considered appropriate to use only one independent claim in any category.

.The Applicant's attention is drawn to the requirements of Article 97 (1) EPC.

2). As far as the subject-matter of the application can be understood from the claims, an invention meeting the requirements of Article 54 and 56 EPC cannot be recog-

nised considering the prior art documents:

D1 = Parfumes, Cosmethiques, Aromes, no. 72, 12/86 "Les masques de beauté" (see page 61, column 3, paragraph 4 - page 63);
D2 = EP-A-0323652 (see the claims);
D3 = US-A-4126142 (see the abstract);
D4 = JP-A-55127312 (see the abstract);
D5 = JP-A-6335511 (see the abstract);
D6 = JP-A-6357508 (see the abstract);
D7 = GB-A-2144133 (see the examples 2,4,7,D); and
D8 = WO-A-9002774 (see the claims).

It has to be stated that the use of polymers having a salt forming group in composition for the treatment and cleansing of skin was already well known in the art before the filing date of the present application.

3). It is not at present apparent which part of the application could serve as a basis for a new, allowable claim. Should the applicant nevertheless regard some particular matter as patentable an independent claim including such matter should be filed taking account of Articles 52(1), 54, 56, 84, 123(2) and Rule 29(1) EPC. The applicant should also indicate in the letter of reply the difference of the subject-matter of the new claim vis-à-vis the state of the art and the significance thereof.

4). The following matters should also receive attention:

.The subject-matter of claim 18 concerns a method for treatment of the human or animal body by surgery or therapy (see also the present description page 1, the

last line of the second paragraph). Consequently, claim 18 does not meet the requirements according to Article 52 (4) EPC, amendment is therefore requested.

.The description must be brought into conformity with the new claims to be filed; care should be taken during revision, especially of the introductory portion including any statements of problem or advantage, not to add subject-matter which extends beyond the content of the application as originally filed, Article 123(2) EPC.

.When amending the claims the Applicant is requested (according to the EPC-Guidelines E-II.1) to identify those passages in the specification as originally filed on which the amended claims are based. In connection with this, the Applicant's attention is drawn to the fact that violation of Article 123 (2) EPC is a ground for refusal of an application (Article 97 (1) EPC).

.The Applicant is requested to file the amendments by way of replacement pages, avoiding unnecessary recasting of the description.